

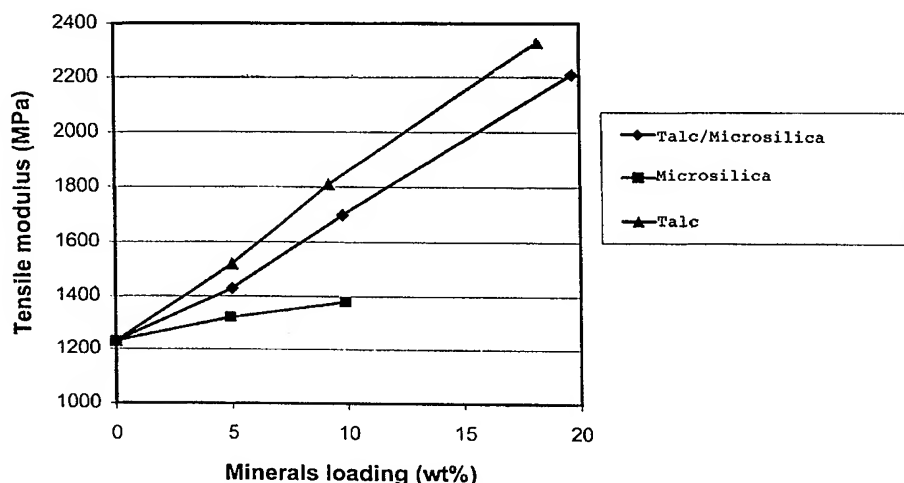


INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C08K 3/34, 3/36		A1	(11) International Publication Number: WO 00/27911
			(43) International Publication Date: 18 May 2000 (18.05.00)
(21) International Application Number: PCT/NO99/00336 (22) International Filing Date: 8 November 1999 (08.11.99) (30) Priority Data: 19985211 9 November 1998 (09.11.98) NO (71) Applicants (for all designated States except US): ELKEM ASA [NO/NO]; Hoffsvæien 65B, N-0377 Oslo (NO). MONDO MINERALS OY [FI/FI]; Laurinmäenkuja 3B, FIN-00440 Helsinki (FI). (72) Inventors; and (75) Inventors/Applicants (for US only): DANIELSSEN, Tore [NO/NO]; Åsveien 20, N-4621 Kristiansand (NO). LIN-NEBO, Anne, Kathrine [NO/NO]; Nedre Frydendal 106, N-1370 Asker (NO). SANDELIN, Bjørn [FI/FI]; Käenpolku 3, FIN-87400 Kajaani (FI). (74) Agent: VINDENES, Magne; Elkem ASA Patent Dept., P.O. Box 8040 Vågsbygd, N-4675 Kristiansand (NO).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	

(54) Title: RESIN COMPOSITIONS, METHOD OF PRODUCING RESIN COMPOSITIONS AND FILLER BLENDS FOR USE IN RESIN COMPOSITIONS

Stiffness of talc/EMS in PP copolymer



(57) Abstract

The present invention relates to thermoplastic resin compositions, particularly polyolefines, polyvinylchloride and polyamide. The thermoplastic resin compositions contain between 3 and 400 % by weight of filler based on the weight of the resin, said filler comprising talc and microsilica where the weight ratio between talc and microsilica is between 15:1 and 1:15. The invention further relates to a method for the production of thermoplastic resin compositions, and to a filler blend for use in thermoplastic resins, said blend containing talc and microsilica in a weight ratio between 15:1 and 1:15.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakistan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

Title of Invention

Resin compositions, method of producing resin compositions and filler blends for use in resin compositions.

5 **Technical Field**

The present invention relates to new and improved resin compositions and more particularly to thermoplastic resin compositions such as polyolefines, polyvinylchloride and polyamide, and to a method for the production of resin compositions. The invention further relates to a filler blend for use in the
10 production of resin compositions.

Background Art

It is well known to produce polyolefines such as polypropylene compound containing functional fillers such as fine particulate talc to increase the
15 stiffness of the final polypropylene product.

Talc is hydrated magnesium silicate with the theoretical formula $3\text{MgO} \cdot 4\text{SiO}_4 \cdot \text{H}_2\text{O}$ and consists of magnesiumhydroxide sandwiched between two sheets of silica.
20

When adding other fillers in addition to talc in order to improve other properties, such as for example impact strength, it has, however, been found that the stiffness obtained by using talc alone as a filler is substantially reduced when adding a second filler for increasing the impact strength. It has
25 therefore not been possible to produce polypropylene products with both a high stiffness and a high impact strength. High stiffness and high impact strength is particularly important in some polypropylene products such as for example car bumpers. The same is true for other thermoplastic resin products.
30

The term thermoplastic resin used in the specification and claims includes not only thermoplastic resins per se, but also mixtures thereof, as well as a blend

of thermoplastic resins with other materials such as an elastomer like nitrile rubber. The so-called thermoplastic rubbers, thermoplastic elastomers are also included in the definition of thermoplastic resin. Thermoplastic resins per se includes polyolefines, polystyrene, polyesters, ABS copolymers, polyvinyl chloride (PVC), unplasticized polyvinyl chloride (UPVC), polyamide, acrylic polymers, polycarbonate polymers, polysulfone polymers and others.

It is known from US patent No. 4,722,952 that the addition of microsilica to polyvinylchloride, improves the impact strength of polyvinylchloride used for the production of electrical conduits. For such products the stiffness is of no importance. On the contrary, high stiffness is not desired for electrical conduits.

The term microsilica used in the specification and claims is particulate amorphous SiO_2 obtained from a process in which silica is reduced and the reduction product is oxidized in vapor phase to form amorphous silica. Microsilica may contain at least 70 % by weight silica (SiO_2) and have a specific density of 2,1 - 2.3 g/cm^3 and a surface area at 15 - 30 m^2/g . The primary particles are substantially spherical. The primary particles have an average size of about 0,15 μm . Microsilica is preferably obtained as a co-product in the production of silicon or silicon alloys in electric reduction furnaces. In these processes large quantities of silica are formed as SiO_2 . The SiO_2 is recovered in conventional manner using filter or other collection apparatus. For the purpose of the present invention the term microsilica also shall be understood to include fly-ash, and more particularly fly-ash particles of substantial spherical shape having a particle size below 10 microns.

Disclosure of Invention

It is an object of the present invention to provide thermoplastic resins having both high stiffness and high impact strength.

According to a first aspect, the present invention thus relates to thermoplastic resin compositions, particularly polyolefines, polyvinylchloride and polyamide, characterized in that the thermoplastic resin compositions contains between 3 and 400 % by weight of filler based on the weight of the resin, said filler comprising talc and microsilica where the weight ratio between talc and microsilica is between 15:1 and 1:15.

According to a preferred embodiment the weight ratio of talc and microsilica is between 6:1 and 1:5.

According to a second aspect the present invention relates to a method for the production of thermoplastic resin composition, particularly polyolefines, polyvinylchloride and polyamide, which method being characterized in that talc and microsilica is added to thermoplastic resin in a total amount between 3 and 400 % by weight based on the weight of thermoplastic resin and where the weight ratio between talc and microsilica is kept between 15:1 and 1:15, whereafter the mixture is formed into a thermoplastic resin product or compound.

According to a preferred embodiment of the method of the present invention talc and microsilica are added to the thermoplastic resin as a mixture of talc and microsilica.

The compounding of the thermoplastic resin can be done using conventional processes like extrusion, calendering, injection moulding and others.

According to a third aspect, the present invention relates to a filler blend for use in thermoplastic resins, particularly polyolefines, polyvinylchloride and polyamide, wherein the filler blend contains talc and microsilica in a weight ratio between 15:1 and 1:15, and particularly between 6:1 and 1:5.

It has surprisingly been found that the combined use of talc and microsilica as fillers in thermoplastic resins, particularly in polyolefines, polyvinylchloride and polyamide, give final products having both high stiffness and high impact strength.

5

EXAMPLE 1

A non-filled polypropylene copolymer "BA 202E" supplied by Borealis was extruded in a compounding extruder with addition of a filler blend consisting of talc supplied by Mondo Minerals OY and microsilica supplied by Elkem ASA. The weight ratio between talc and microsilica in the filler blend was 2:1 and tests were run with addition of 5, 10 and 19 % by weight of the filler blend based on the weight of the polypropylene copolymer. The stiffness of the extruded polypropylene was measured as tensile modulus according to ISO 527 and the impact strength of the extruded polypropylene was measured as notched charpy impact strength according to ISO 179/1A.

For comparison purposes the polypropylene copolymer was extruded in the compounding extruder with no addition of filler and with the addition 5, 10 and 18 % by weight of talc and with 5 and 10 % by weight of microsilica. Also for these comparative tests the stiffness and the impact strength were measured as stated above. The resulting stiffness and impact strength are shown in figure 1 and figure 2 respectively.

As can be seen from figure 1 and 2, the impact strength of the polypropylene containing both talc and microsilica is much higher than for the polypropylene containing only talc and only slightly lower than for the polypropylene containing only microsilica as a filler. The stiffness of the polypropylene containing both talc and microsilica is much higher than for polypropylene containing only microsilica as a filler and only slightly lower than for polypropylene containing only talc as a filler. The use of a blend of talc and

microsilica thus surprisingly gives a polypropylene having both a high stiffness and a high impact strength.

EXAMPLE 2

A non-filled high density polyethylene (HDPE) copolymer "HDPE HE 2467-BL" supplied by Borealis was extruded in a compounding extruder with addition of a filler blend consisting of talc supplied by Mondo Minerals OY and microsilica supplied by Elkem ASA. The weight ratio between talc and microsilica in the filler blend was 2:1 and the test was run with addition of 10 % by weight of the filler blend based on the weight of the HDPE copolymer. The stiffness of the extruded HDPE was measured as tensile modulus according to ISO 527 and the impact strength of the extruded HDPE was measured as notched charpy impact strength according to ISO 179/1A.

For comparison purposes the HDPE copolymer was extruded in the compounding extruder with no addition of filler, with the addition 10 % by weight of talc and with addition of 10 % by weight of microsilica. Also for these comparative tests the stiffness and the impact strength were measured as stated above. The resulting stiffness and impact strength are shown in table 1.

Table 1

Material	Tensile Modulus (MPa)	Impact Strength (kJ/m²)
HDPE nonfilled	850	13.6
HDPE + 10 % talc	1160	18.0
HDPE + 10 % microsilica	880	27.6
HDPE + 10 % filler blend	1070	22.3

As can be seen from table 1, the impact strength of the HDPE containing both talc and microsilica is higher than for the HDPE containing only talc, but lower than for the HDPE containing only microsilica as a filler. The stiffness of the HDPE containing both talc and microsilica is much higher than for HDPE containing only microsilica as a filler and only slightly lower than for HDPE containing only talc as a filler. The use of a blend of talc and microsilica thus surprisingly resulting in a HDPE having both a high stiffness and a high impact strength.

EXAMPLE 3

A non-filled polyvinylchloride (PVC) polymer was calendered with addition of a filler blend consisting of talc supplied by Mondo Minerals OY and microsilica supplied by Elkem ASA. The weight ratio between talc and microsilica in the filler blend was 2:1 in one run and 1:2 in another run, and the tests were run with addition of 5 % by weight of the filler blend based on the weight of PVC polymer. The stiffness of the calendered PVC was measured as tensile modulus according to ISO 527 and the impact strength of the calendered PVC was measured as notched charpy impact strength according to ISO 179/1A.

For comparison purposes the PVC polymer was calendered with no addition of filler, with addition of 5 % by weight of talc and with addition of 5 % by weight of microsilica. Also for these comparative tests the stiffness and the impact strength were measured as stated above. The resulting stiffness and impact strength are shown in table 2.

Table 2

Material	Tensile Modulus (MPa)	Impact Strength (kJ/m²)
PVC nonfilled	2916	6.5
PVC + 5 % talc	3484	5.4
PVC + 5 % microsilica	3010	8.5
PVC + 5 % filler blend talc/microsilica 2:1	3360	5.1
PVC + 5 % filler blend talc/microsilica 1:2	3167	7.9

As can be seen from table 2, the impact strength of PVC containing talc and microsilica in a ratio of 2:1 is about the same as for the PVC containing only talc, but lower than for PVC containing only microsilica as a filler. For PVC containing talc and microsilica in a ratio of 1:2 it can be seen that the impact strength is higher than for PVC containing talc and microsilica in a ratio of 2:1 and almost as high as for PVC containing only microsilica. The stiffness of the PVC containing talc and microsilica in a ratio of 2:1 is much higher than for PVC containing only microsilica as a filler and only slightly lower than for PVC containing only talc as a filler. For PVC containing talc and microsilica in a ratio of 1:2 it will be seen that the tensile modulus is still higher than for PVC containing only microsilica. The use of a blend of talc and microsilica thus surprisingly gives a PVC having both a high stiffness and a high impact strength.

EXAMPLE 4

A non filled polyamide (PA) polymer, "PA6 Ultramid B35" delivered by BASF was extruded in a compounding extruder with addition of a filler blend consisting of talc supplied by Mondo Minerals OY and microsilica supplied by

Elkem ASA. The addition of filler blend was 10 % by weight of polymer. The weight ratio between talc and microsilica in the filler blend in a first test was 1:1 and 1:2 in a the second test. The stiffness of the extruded PA was measured as tensile modulus according to ISO 527 and the impact strength of the extruded PA was measured as notched charpy impact strength according to ISA 179/1A.

For comparison purposes the PA copolymer was extruded in the compounding extruder with no addition of filler, with the addition 10 % by weight of talc and with addition of 10 % by weight of microsilica. Also for these comparative tests the stiffness and the impact strength were measured as stated above. The resulting stiffness and impact strength are shown in table 3.

Table 3

Material	Tensile Modulus (MPa)	Impact Strength (kJ/m²)
PA nonfilled	700	Non-break
PA + 10 % talc	1430	10.6
PA + 10 % microsilica	890	33.2
PA + 10 % filler blend talc/microsilica 1:1	1210	16.3
PA + 10 % filler blend talc/microsilica 1:2	1120	19.7

As can be seen from table 3, the impact strength of the PA containing both talc and microsilica is much higher than for the PA containing only talc, but lower than for the PA containing only microsilica as a filler. It can also be seen that the impact strength increases with increasing amount of microsilica in the filler blend. The stiffness of the PA containing both talc and microsilica is

much higher than for PA containing only microsilica, but the stiffness is slightly reduced when the microsilica content in the filler blend is increased.

CLAIMS

- 5 1. Thermoplastic resins compositions, particularly polyolefines, polyvinylchloride and polyamide, characterized in that the thermoplastic resin compositions contain between 3 and 400 % by weight of filler based on the weight of the resin, said filler comprising talc and microsilica where the weight ratio between talc and microsilica is between
10 15:1 and 1:15.
2. Thermoplastic resins according to claim 1, characterized in that the weight ratio of talc and microsilica is between 6:1 and 1:5.
- 15 3. A method for the production of thermoplastic resin composition, particularly polyolefines, polyvinylchloride and polyamide, characterized in that talc and microsilica is added to the thermoplastic resin in a total amount between 3 and 400 % by weight based on the weight of thermoplastic resin and where the weight ratio between talc and microsilica is
20 kept between 15:1 and 1:15, whereafter the mixture is formed to a thermoplastic resin product or compound.
4. A method according to claim 3, characterized in that talc and microsilica are added to the thermoplastic resin as a mixture of talc and
25 microsilica.
5. A method according to claim 2, characterized in that talc and microsilica are added separately to the thermoplastic resin.
- 30 6. A filler blend for use in thermoplastic resin compositions, particularly polyolefines, polyvinylchloride and polyamide, characterized in

that the filler blend contains talc and microsilica in a weight ratio between 15:1 and 1:15.

7. A filler blend according to claim 6, characterized in that the
5 filler blend contains talc and microsilica in a weight ratio between 6:1 and 1:5.

Stiffness of talc/EMS in PP copolymer

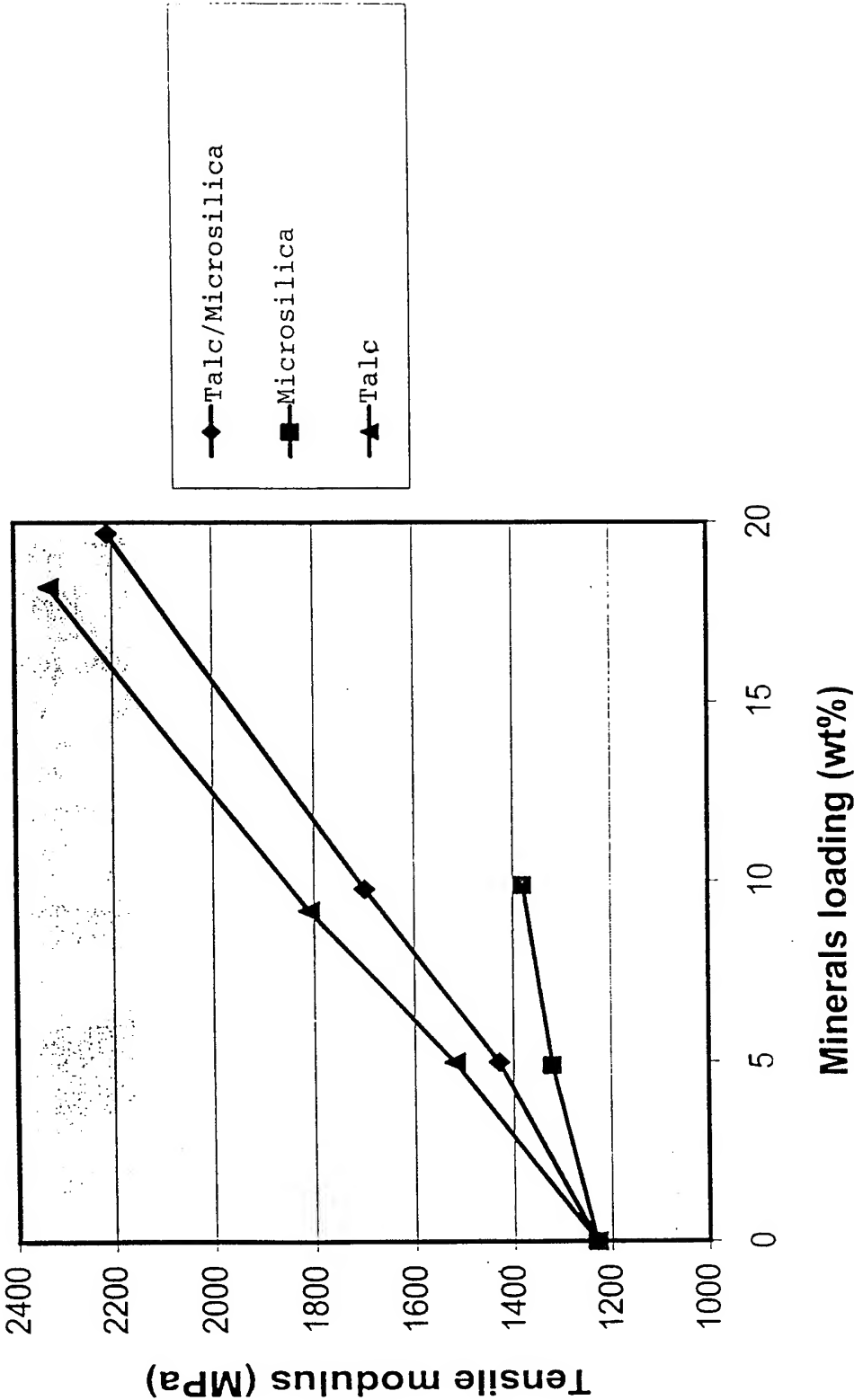


FIGURE 1

2/2

Impact strength of talc/EMS in PP copolymer

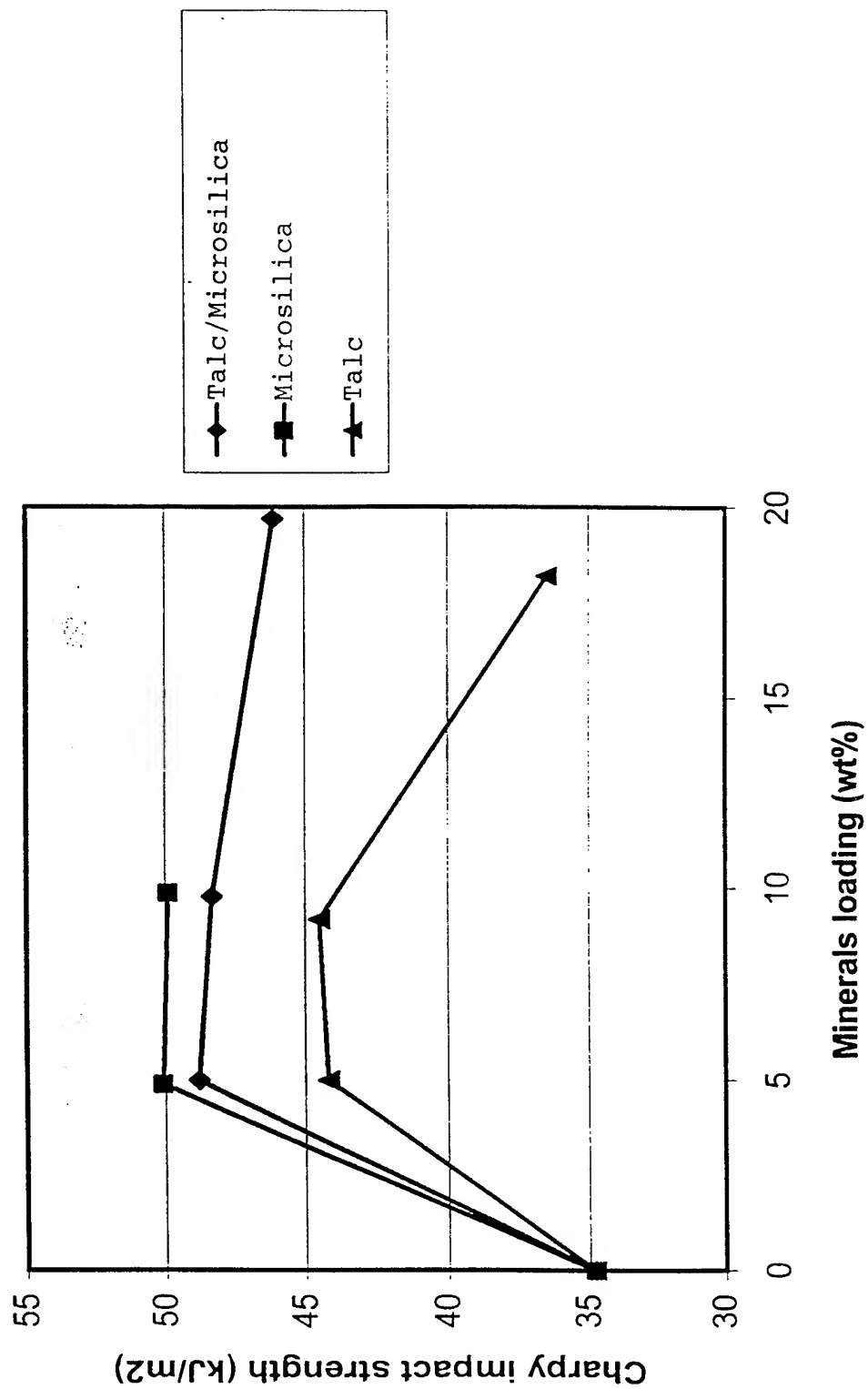


FIGURE 2

INTERNATIONAL SEARCH REPORT

International application No.

PCT/NO 99/00336

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C08K 3/34, C08K 3/36

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4956404 A (JOSEF PELZIG), 11 Sept 1990 (11.09.90), column 4, line 5 - line 14; column 5, line 3 - line 7; column 6, line 1 - line 39, claims 1,12, abstract --	1-7
A	US 5266609 A (NEIL R. HALL ET AL), 30 November 1993 (30.11.93), column 3, line 17 - line 30, claims 1,9 and 12 --	1-7
A	US 4714733 A (KUNIO ITOH ET AL), 22 December 1987 (22.12.87), column 6, line 25 - line 38, abstract --	1-7

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

13 March 2000

Date of mailing of the international search report

19-04-2000

Name and mailing address of the ISA/

Swedish Patent Office

Box 5055, S-102 42 STOCKHOLM

Facsimile No. +46 8 666 02 86

Authorized officer

Barbro Nilsson/Els

Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT

International application No.

PCT/NO 99/00336

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4722952 A (BRIAN W. HATT), 2 February 1988 (02.02.88), abstract --	1-7
A	US 4140669 A (DONALD L. PHIPPS, JR. ET AL), 20 February 1979 (20.02.79), abstract --	1-7
A	Patent Abstracts of Japan, abstract of JP 83-37059 A (NEW OJI PAPER CO LTD.), 24 December 1996 (24.12.96) -- -----	1-7

INTERNATIONAL SEARCH REPORT

Information on patent family members

02/12/99

International application No.

PCT/NO 99/00336

Patent document cited in search report			Publication date	Patent family member(s)		Publication date
US	4956404	A	11/09/90	NONE		
US	5266609	A	30/11/93	AT	142665 T	15/09/96
				AU	627552 B	27/08/92
				AU	5031290 A	24/08/90
				CA	2026009 A	28/07/90
				DE	69028488 D,T	13/02/97
				DK	429556 T	17/02/97
				EP	0429556 A,B	05/06/91
				SE	0429556 T3	
				ES	2095248 T	16/02/97
				JP	3504874 T	24/10/91
				WO	9008799 A	09/08/90
US	4714733	A	22/12/87	DE	3786252 A,T	22/07/93
				EP	0278157 A,B	17/08/88
				JP	1818419 C	27/01/94
				JP	5028732 B	27/04/93
				JP	63199253 A	17/08/88
US	4722952	A	02/02/88	NONE		
US	4140669	A	20/02/79	AU	527220 B	24/02/83
				AU	4301678 A	05/07/79
				CA	1127787 A	13/07/82
				DE	2854751 A	12/07/79
				FR	2413434 A,B	27/07/79
				GB	2011439 A,B	11/07/79
				JP	54100449 A	08/08/79
				NL	7812417 A	03/07/79